

# STORAGE STABILITY OF DIESEL FUEL PRODUCED FROM BRAZILIAN CRUDE - CHEMICAL MODIFICATION DURING AGEING AND THE EFFECT OF HYDROTREATING ON FUEL STABILITY

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## INTRODUCTION

The growing need for diesel fuels and developments in refining processes, particularly the increased use of Fluid Catalytic Cracking (FCC), have led refiners to introduce Light Cycle Oil (LCO) in diesel formulations. Unfortunately, the cracking products, which contain chemically unstable species (1,2), induce changes in color and insolubles formation, even when diluted by blending. The insolubles are known to cause operability problems in diesel engines (3).

Degradation mechanisms are complicated and not well understood. It seems that oxidation plays a determining role (4). Acids such as carboxylic, sulfonic and phenolic, produced by oxidation of fuels have been considered to exert a catalytic effect on the quantity of sediment formed (5). It was demonstrated that aromatic compounds and non-basic nitrogen compounds are also involved in sediment formation (6). Pedley et al. (7,8) found that a major source of strongly colored sediments could be the reaction of oxidized products with alkyl indoles, yielding addition products that precipitate under the influence of sulfonic acids, produced by oxidation of thiols.

The nitrogen compounds present in LCO were largely identified (9) and included anilines, alkyl indoles and alkyl carbazoles. It seems that only the alkyl indoles are subject to changes during degradation in storage (10).

A large number of tests have been used to predict stability of middle distillates. The ASTM D 4625 has widespread acceptance for its good correlation with storage at ambient conditions (11). The new accelerated test method, ASTM D 5304, shows excellent correlation with lower temperature tests (12).

The principal processes used to improve fuel stability include hydrotreatment and the use of additives. Schrepfer et al. (13) reported that although hydrotreating is the most effective method of minimizing stability problems, it is also the most costly.

Some characteristics of Marlim crude oil such as high nitrogen content and low middle distillate yield, have led us to anticipate problems on diesel stability with the beginning of Marlim oil processing.

The purposes of this study were to estimate the impact on storage stability behaviour of diesel fuels and to evaluate: 1- the effect of the mildest Petrobrás hydrotreatment unit on fuel stability, in particular with respect to non-basic nitrogen compounds; 2- the influence of hydrotreating and the use of additive; 3- the changes in phenalenone, pyrrolic nitrogen, basic nitrogen, mercaptans, alkyl indoles, acidity during ageing at 43 °C for periods of up to 12 weeks.

## EXPERIMENTAL

Nine experimental diesel fuel samples were made up from several streams obtained in the Marlim crude processing. Their composition is shown in Table 1. The physico-chemical characteristics of selected samples are shown in Table 2. A total of 20 liters of each component was stored at low temperature under nitrogen blanket to prevent degradation before analyses.

### Effect of hydrotreating on fuel stability

Hydrotreating was performed on two feedstocks, a straight run distillate (A2) and a blend (A2/B), in the following operating conditions: LHSV: 1,5 h<sup>-1</sup>; Temperature: 320 °C; H<sub>2</sub> Partial pressure: 29 bar. The method ASTM D 5304 (Assessing Distillate Fuel Storage Stability by Oxygen Overpressure) was used to evaluate the effect of hydrotreating on improving fuels stability. The reported total insolubles values are averages of duplicate analyses. Additionally, color determinations were made before and after ageing according to ASTM D 1500.

The "pyrrolic" nitrogen compounds were separated from the samples by HPLC using basic and acidic alumina columns, based on procedures described by Boduszynski (14). The

isolated compounds were identified by GC/MS. The quantification was conducted by GC-FID using carbazole as internal standard.

#### **Kinetics of ageing at 43 °C in air**

In order to better understand the mechanisms of sediment formation in fuels produced from Marlim oil, kinetic analyses were performed in the raw LCO (B) and in the three following blends: A1/A2/B; A1/A2/AD-B; A1/HT-(A2/B). An antioxidant containing tertiary amines and metal deactivator in its formulation was added to the hot LCO. Storage stability of each fuel sample was assessed by ASTM D 4625 (Distillate Fuel Storage Stability at 43 °C for 12 weeks). The reported total insolubles values are averages of triplicate analyses. Additionally, color determinations were made before and after ageing according to ASTM D 1500.

To follow the kinetics of the blends a total of 1000 ml of each fuel was placed in amber glass bottles of the same volume and the bottles closed with vented screw caps. Six bottles of each fuel were aged concurrently in a dark room at  $43 \pm 1$  °C, in contact with atmospheric air, for periods of up to twelve weeks. After every two weeks, one bottle of each fuel was removed and allowed to cool to ambient temperature. All samples were protected from light before, during and after ageing. The filterable insolubles were determined by vacuum filtration of 300 ml of each aged fuel, through two preweighted cellulose acetate filters (0,8 µm porosity). The filters were then rinsed with isooctane to remove traces of fuel, removed from the filter support assembly, oven dried (90 °C), cooled to ambient temperature in a desiccator and reweighted. The fuel samples were also analysed for color degradation, changes in phenalenone, pyrrolic nitrogen, basic nitrogen, mercaptans, alkyl indoles and total acid number.

The concentration of phenalenone was determined by normal phase HPLC with UV detection and direct injection of the sample, based on procedure described by Marshman (15). Concentrations of phenalenone up to 0,5 mg/l could be determined by this methodology.

The changes in alkyl indoles were monitored using a capillary gas chromatograph (CG) with selective detection by isobutane chemical ionization mass spectrometry (16). The method is based on the fact that the carbazole remains relatively unaffected during ageing, as verified by some authors (10). The evolution of alkyl indoles was then determined through changes in the ratios of alkyl indoles/carbazole peak areas.

## **RESULTS AND DISCUSSION**

### **Effect of hydrotreating on fuel stability**

The effect of hydrotreating on fuel stability assessed by ASTM D 5304 is presented in Table 3. The degrees of hydrodesulfurization (HDS) and hydrodenitritification (HDN) are also indicated. The hydrotreating process improved color stability of both samples, however complete stabilization was not achieved. On the other hand, the A2/B blend was stabilized in terms of insolubles formation.

As can be seen in Table 4, the alkyl indoles were partially removed while the alkyl carbazoles remained in the original levels. Additionally, a decrease in other species such as acids and mercaptans, that are supposed to contribute to degradation, was observed. Based on these results, it is confirmed that alkyl indoles and acidity play an important role on sediment formation and that stabilization of the fuel can be achieved by hydrotreating even at mild severity, without requiring total removal of nitrogen compounds. Under low  $H_2$  partial pressure, the fuel chemical composition is not deeply modified, mainly with regard to nitrogen and aromatic content.

### **Kinetics of ageing at 43 °C in air**

The results related to color changes and total insolubles formation using ASTM D 1500 and ASTM D 4625 are presented in Figures 1 and 2, respectively. The raw LCO (B) is unstable mainly with respect to color degradation. A low formation of insolubles were observed, with the majority of insolubles in the adherent form. This behaviour drastically changed when the raw LCO was added to straight run distillates (A1,A2), as can be seen through the A1/A2/B blend results. In this sample, there was extensive formation of insolubles (mostly filterable insolubles) and color degradation. The contribution of the straight run distillates components in terms of acidity seems to exert a great influence on the sediment formation. From the results of the blend with additive it can be concluded that the antioxidant was ineffective on improving fuel stability. On the other hand, the blend containing hydrotreated components exhibited satisfactory results with total insolubles content of 0,2 mg/100 ml. The color degradation was minimized but was not completely eliminated.

The results obtained from the kinetics of ageing are summarized in Table 5. As can be seen, the phenalene concentrations increased rapidly during the first two weeks of ageing, levelling off thereafter in the following samples: B, A1/A2/B and A1/A2/AD-B. It is difficult to conclude if this stabilization was a result of the balance between consumption and production of phenalene during the overall mechanism of sediment formation or was due to occurrence of degradation before the ageing at 43 °C. There appears to be a correlation between color degradation and phenalene concentration since color degradation also reached the maximum value during the first two weeks. All the samples exhibited decrease in the pyrrolic nitrogen concentration and in the ratio alkyl indoles/carbazole. The decrease agrees with the relationship between the reactivity of the alkyl indoles and the filterable insolubles formation. According to this observation it can be concluded that: 1- the degradation mechanism proposed by Pedley et al. seems to be the major source of sediment formation in samples containing LCO, 2- the additive tested was ineffective to prevent phenalene oxidation and the progressive consumption of alkyl indoles. Hydrotreating appears to remove phenalenes since phenalenes were not detected in A1/HT-(A2/B) blend. The decreases in the pyrrolic nitrogen and in the ratio alkyl indoles/carbazole were also verified in a lower extent comparing to the others samples. The mercaptans and the total acid number remained practically unaltered during the ageing. These observations suggest that exists a correlation between the insoluble formation and the alkyl indoles disappearance and that other different mechanism of degradation from the proposed by Pedley takes place. It confirms, as previously demonstrated by some authors (17), that the removal of phenalenes, indoles or acids, will result in a stable fuel.

## CONCLUSIONS

On the whole, the experimental fuels obtained from Marlum oil presented poor stability. The addition of light cycle oil in the straight run distillate, to increase the yield of diesel fuel, was not satisfactory inducing higher levels of insolubles and color degradation.

The results of ASTM D 4625 and kinetics study showed that the additive was ineffective on preventing phenalene oxidation and the progressive disappearance of alkyl indoles. Similar levels of insolubles formation and color degradation was verified in the fuel in presence and absence of the additive. In both samples it seems that the major mechanism of degradation was similar to the proposed by Pedley et al..

The hydrotreating, even at mild operating conditions, improved substantially the stability properties of the fuel. Under the tested conditions the hydrodenitritication was not complete, just only partial alkyl indoles elimination has occurred. Hydrotreating also appears to remove species that are considered to contribute to the degradation of the fuel, such as, acids, mercaptans and phenalenes. This study suggests that in this case, other mechanisms of degradation are taking place and confirms earlier findings that the major mechanism of fuel degradation depends above all on the composition of the fuel.

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**Table 1 - Composition of the samples**

Samples	Composition
A1	100 vol. % straight run distillate
A2	100 vol. % straight run distillate
HT-A2	100 vol. % hydrotreated A2
B	100 vol. % raw catalytically cracked cycle oil (LCO)
A2/B	84 vol. % A2 + 16 vol. % B
HT-(A2/B)	Hydrotreated A2/B
A1/A2/B	36 vol. % A1 + 54 vol. % A2 + 10 vol. % B
A1/A2/AD-B*	36 vol. % A1 + 54 vol. % A2 + 10 vol. % AD-B
A1/HT-(A2/B)	36 vol. % A1 + 64 vol. % HT-(A2/B)

a - hot LCO plus additive (tertiary amines and metal deactivator)

**Table 2 - Physico-chemical characteristics**

Characteristics	Method	A1	A2	HT-A2	B	A2/B	HT-(A2/B)
Specific gravity at 20/4 °C	ASTM D 1298	0,8544	0,8940	0,8918	0,8438	0,9050	0,8986
Distillation IBP/EBP, °C	ASTM D 88	217/313	110/402	132/ -	208/314	208/402	230/ -
Color	ASTM D 1500	1,0	2,5	L 1,5	4,0	3,0	1,5
Total acid number, mg KOH/g	ASTM D 674	0,54	1,50	0,02	0,04	1,10	0,04
Sulfur, wt. %	ASTM D 2822	0,33	0,58	0,21	0,70	0,59	0,18
Mercaptans, mg/kg	ASTM D 3227	10	26	7	28	30	6,2
Total nitrogen, mg/kg	ASTM D 4629	110	1100	1000	2000	1200	980
Basic nitrogen, mg/kg	UOP 269	110	616	530	445	470	430
Pyrrolic nitrogen, mg/l	UOP 276	-	18,1	18,7	989	170	99,2
% C aromatic	NMR	-	20,1	21,8	63,8	31,7	27,5

**Table 3 - Stability of hydrotreated fuels**

Heteroatoms removal	A2	HT-A2	A2/B	HT-A2/B
HDN, %	-	9	-	18
HDS, %	-	64	-	68
Stability test - ASTM D 5304				
ASTM color before test	L 2,5	L 1,5	L 3,5	L 1,5
ASTM color after test	L 8,0	L 3,5	L 8,0	L 3,5
Total insolubles, mg/100 ml	0,7	0,5	8,2	0,6
Pass/Fail criteria (max.)	IT 4,0	mg/100 ml	Color after	3,0

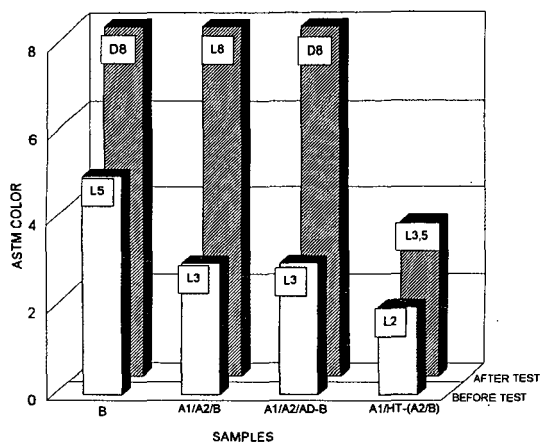
Table 4 - Changes in pyrrolic nitrogen compounds with hydrotreating

Compounds, µg/g	A2	HT- A2	A2/B	HT-(A2/B)
<b>Alkyl indoles</b>	<b>ND<sup>a</sup></b>	<b>ND</b>	<b>2022</b>	<b>1061</b>
C <sub>0</sub> <sup>a</sup>	ND	ND	41	7
C <sub>1</sub>	ND	ND	327	82
C <sub>2</sub>	ND	ND	722	294
C <sub>3</sub>	ND	ND	669	441
C <sub>4</sub>	ND	ND	263	237
<b>Alkyl carbazoles</b>	<b>2328</b>	<b>2074</b>	<b>2111</b>	<b>1916</b>
C <sub>0</sub>	ND	ND	55	49
C <sub>1</sub>	81	66	168	174
C <sub>2</sub>	350	313	395	355
C <sub>3</sub>	685	615	571	498
C <sub>4</sub>	832	750	644	593
C <sub>5</sub>	380	330	278	247

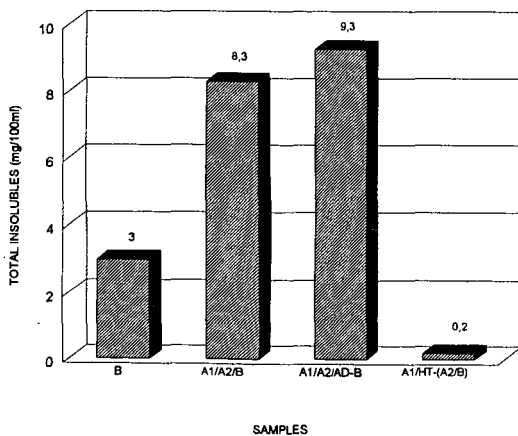
a - Subscript designates total number of carbons in alkyl groups.  
b - non detected.

Table 5 - Ageing kinetics at 43 °C

Characteristics			B	A1/A2/B	A1/A2/AD-B	A1/HT-(A2/B)
ASTM color	WEEKS	0	L 5,0	L 3,0	L 3,0	L 2,0
		2	D 8,0	L 7,5	L 8,0	L 2,5
		4	D 8,0	D 8,0	L 8,0	L 3,5
		6	D 8,0	D 8,0	D 8,0	L 3,5
		8	D 8,0	D 8,0	D 8,0	L 4,0
		10	D 8,0	L 8,0	L 8,0	L 3,5
		12	D 8,0	L 8,0	D 8,0	L 3,5
Filterable insolubles, mg/100ml	WEEKS	0	0,4	0,0	0,5	0,2
		2	0,2	3,2	3,3	0,3
		4	0,7	3,8	4,6	0,1
		6	0,9	5,2	5,8	0,5
		8	0,4	2,8	1,6	0,0
		10	1,1	5,5	2,8	0,5
		12	1,6	6,9	7,8	0,4
Basic nitrogen, mg/kg	WEEKS	0	600	425	380	365
		2	525	350	415	330
		4	415	370	390	350
		6	460	430	425	360
		8	400	350	360	300
		10	565	360	375	330
		12	550	365	370	320
Pyrrolic nitrogen, mg/l	WEEKS	0	737	83,4	87,1	66,8
		2	743	71,4	78,8	63,3
		4	749	65,3	70,6	65,7
		6	696	63,0	64,3	62,4
		8	744	59,2	69,1	63,4
		10	680	57,4	60,3	61,2
		12	686	57,1	56,1	59,6
Mercaptans, mg/kg	WEEKS	0	13	17	23	7,5
		2	5,0	15	15	7,5
		4	5,5	14	14	7,5
		6	5,5	11	12	7,5
		8	3,0	9,0	9,0	6,0
		10	3,0	9,0	9,0	7,0
		12	3,0	8,0	7,0	7,0
Total acid number, mg KOH/g	WEEKS	0	0,01	0,98	0,98	0,20
		2	0,02	0,94	0,93	0,18
		4	0,02	1,05	1,05	0,18
		6	0,02	0,95	0,95	0,19
		8	0,02	0,95	0,94	0,17
		10	0,02	0,93	0,92	0,20
		12	0,04	0,95	0,94	0,19
Phenalenone, mg/l	WEEKS	0	49,9	5,1	4,3	< 0,5
		2	169,4	8,0	9,2	< 0,5
		4	269,4	7,4	8,2	< 0,5
		6	294,8	7,1	8,1	< 0,5
		8	291,7	6,9	7,6	< 0,5
		10	296,9	7,0	7,8	< 0,5
		12	285,8	7,0	8,4	< 0,5
Alkyl indoles/ carbazole	WEEKS	0	98,7	48,5	50,3	26,5
		2	82,7	39,4	38,3	24,2
		4	72,8	37,5	33,5	25,1
		6	-	-	-	-
		8	77,3	35,2	28,6	22,2
		10	-	-	-	-
		12	64,5	32,5	26,4	21,0



**Figure 1 - Results of color changes before and after ASTM D 4625**



**Figure 2 - Results of total insolubles of ASTM D 4625**